# UNIMOLECULAR REACTIONS

## A Concise Introduction

The statistical theory of unimolecular reactions is now universally known as RRKM theory. This textbook covers the basics necessary for the understanding of RRKM theory in its original, angular-momentum-conserved, phase-space, and simplified variational incarnations. Discussed are applications of RRKM theory to specific reaction systems, including thermal, chemical-activation, and multi-channel systems.

After a review of the Kassel quantum model and the theory of Slater, the specific-energy RRKM rate constant $k(E)$ is derived. Experimental evidence for (and some against) the RRKM form of $k(E)$ is given. The argument is then extended to the angular-momentum-dependent rate constant $k(E, J)$, to non-classical effects (tunneling and non-adiabatic transitions), the general problem of conservation of angular momentum, and to discussion of exit-channel effects. A chapter is devoted to the counting of quantum states, making extensive use of the Laplace-transform technique and the method of steepest descents. The chapter on thermal systems discusses both analytical and numerical solutions based on the master-equation approach, including activation by black-body radiation of interest in the biomedical field.

The book will be of primary interest to advanced undergraduate and graduate students studying chemical dynamics, chemical kinetics, and theoretical chemistry, as well as to interested researchers in other disciplines wishing to be acquainted with the essentials of RRKM theory.

# UNIMOLECULAR REACTIONS

## A Concise Introduction

WENDELL FORST
*Université Bordeaux I, Talence, France*

CAMBRIDGE
UNIVERSITY PRESS

PUBLISHED BY THE PRESS SYNDICATE OF THE UNIVERSITY OF CAMBRIDGE
The Pitt Building, Trumpington Street, Cambridge, United Kingdom

CAMBRIDGE UNIVERSITY PRESS
The Edinburgh Building, Cambridge CB2 2RU, UK
40 West 20th Street, New York, NY 10011-4211, USA
477 Williamstown Road, Port Melbourne, VIC 3207, Australia
Ruiz de Alarcón 13, 28014 Madrid, Spain
Dock House, The Waterfront, Cape Town 8001, South Africa

http://www.cambridge.org



First published 2003

Printed in the United Kingdom at the University Press, Cambridge

*Typeface* Times 11/14 pt *System* LaTeX 2ε [TB]

*A catalogue record for this book is available from the British Library*

*Library of Congress Cataloguing in Publication data*

Forst, Wendell.
Unimolecular reactions: a concise introduction / Wendell Forst.
p. cm.
Includes bibliographical references and indexes.
ISBN 0 521 82190 8 – ISBN 0 521 52922 0 (pbk.)
1. Unimolecular reactions. 2. Statistical mechanics. I. Title.
QD502.F68 2003 541.3′93–dc21 2003041049

ISBN-13 978-0-521-82190-2 hardback
ISBN-10 0-521-82190-8 hardback

ISBN-13 978-0-521-52922-8 paperback
ISBN-10 0-521-52922-0 paperback

# Contents

# Preface

This textbook is an outgrowth of my *Theory of Unimolecular Reactions*, originally published in 1973 (now out of print), which was rather well received at the time. New developments of the subject since then seem sufficiently numerous and important to justify writing an entirely new text rather than merely updating the old one. Since in the meantime the subject matter has grown considerably, the focus of the present text is narrower, for instance excluding reactions of ionic species *per se* and isotope effects.

The aim of the presentation is a fundamental exposition intended as a graduate-level introduction to this particular field of chemical dynamics. It is primarily concerned with the basics of the theory, and therefore does not deal in much detail with interpretation of experimental results on specific reaction systems, except insofar as they illustrate a given point of theory, given that there are fairly recent publications that discuss such topics. (See R. G. Gilbert and S. C. Smith, *Theory of Unimolecular and Recombination Reactions* (Blackwell Scientific, 1990); K. A. Holbrook, M. J. Pilling and S. H. Robertson, *Unimolecular Reactions*, 2nd Ed. (Wiley, 1996), concerned primarily with thermal reactions; and T. Baer and W. L. Hase, *Unimolecular Reaction Dynamics* (Oxford University Press, 1996), which deals exlusively with state- or energy-selected systems.)

While, for reasons of presenting a coherent argument, some sections of the present work cover more or less the same ground as in these publications, though often from a different point of view, the major emphasis is on detailed treatment of topics not covered elsewhere. There are numerous problems illustrating various ramifications of the arguments developed in the main text, with which the reader can test his or her comprehension. Answers are provided for selected problems.

The subject matter is organized into nine chapters and six appendices. Equations, figures, and problems in each chapter are numbered from 1 onwards, preceded by

the chapter number, separated by a full stop; thus, for example, "eq. (5.25)" refers to equation 25 of Chapter 5.

I am grateful to Professor J.-C. Rayez (Bordeaux) for support, to Professor J. C. Lorquet (Liège) for comments, and to Dr David Husain (Cambridge) who was instrumental in bringing this work to print.

# Symbols

| | |
|---|---|
| $\mathbb{M}$ | matrix |
| $\mathbf{N}$ | vector |
| $\mathfrak{L}$ | Laplace transform |
| $A$, $B$ | rotational constants |
| $E$ | energy |
| $G(E)$ | sum of states at $E$ |
| $J$, $K$ | rotational quantum number |
| $L$ | orbital quantum number |
| $N(E)$ | density of states at $E$ |
| $Q$ | partition function |
| $T$ | temperature |
| $V$ | potential |
| $k$ | Boltzmann's constant |
| $k_{\text{uni}}$ $k_\infty$ $k_0$ | canonical (thermal) rate constant |
| $k(E)$ | microcanonical (specific-energy) rate constant |
| log | logarithm base 10 |
| $\ln$ | natural logarithm |
| $t$ | time |
| $\mu$ | reduced mass |
| $\omega$ | collision frequency (except in Chapter 8) |
| $\Gamma(n)$ | gamma function |

Other symbols have a specific definition in each chapter.